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## THE MINI-CIDEX GC/IMS: ANALYSIS OF COMETARY ICE AND DUST.

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### ABSTRACT

Comets are recognized as among the most scientifically important objects in the solar system. They are presumed relics of the early primitive material in the solar nebula and are believed to have provided a general enrichment of volatiles to the inner solar system. The Cometary Coma Chemical Composition (C4) Mission, a proposed Discovery-Class Mission, will analyze materials released into the coma, providing information leading to the understanding of the chemical composition and make-up of the cometary nucleus. As one of two scientific instruments in the C4 spacecraft, an advanced and streamlined version of the Cometary Ice and Dust Experiment (CIDEX), a mini-CIDEX, will employ an X-Ray Fluorescence (XRF) spectrometer to determine bulk elemental composition of cometary dust grains and a Gas Chromatograph / Ion Mobility Spectrometer (GC/IMS) for determination of the molecular composition of dust and ices following stepwise pyrolysis and combustion. A description of the mini-CIDEX IMS will be provided as well as data from analyses conducted using the mini-CIDEX breadboard instrument.

### INTRODUCTION

Comets are of enormous scientific interest for many reasons. They are primitive bodies that date back to the earliest stages of solar system formation and, because of their small size and because they have been stored in the outer reaches of the solar system, their pristine nature has been preserved better than for any other class of body. They are extremely rich in highly volatile elements, many in the form of ices, and are richer in organic matter than any other known solar system body. It is strongly suspected that in addition to their content of primordial solar nebular material, they also incorporate unprocessed matter from the interstellar medium. Impacts by comets occur onto all the planets and satellites, often with major consequences (e.g., the dinosaur extinction event at the K/T boundary), or sometimes just providing a spectacular cosmic event (e.g., the collision of comet Shoemaker-Levy 9 with Jupiter). Much continues to be learned by ground-based photo and spectroscopic studies of the more than 100 comets that have been perturbed into the inner solar system. Comets have major surface heterogeneities and exhibit a rich diversity of activity due to the emissions and associated plasma phenomena of the comae and tails.

Planetary geochemistry, atmospheric science, astrophysics, cosmochemistry, space physics, interplanetary dust, and exobiology all have a stake in the advances that can be made by reading the chemical tapestry embedded in the cometary nucleus. Comets may have played a strong role in the origin of the atmospheres of the planets, in the compositional content of their crusts, and even in the origin and early evolution of life  $3.5 \times 10^9$  years ago on Earth and the continuing extinction of species since that time.

## The C4 Mission

The Cometary Coma Chemical Composition (C4) Mission, a proposed Discovery class mission, provides a unique opportunity for studying the make up of the cometary nucleus, details of cometary activity, and chemical characteristics of the comet's various morphological and stratigraphic units. C4 can perform the direct *in situ* measurements to provide valuable data to greatly increase our understanding of the nature of comets and provide the key to better interpretations of the continuing program of ground-based observations by astronomers using spectroscopic imaging.

To provide the maximum scientific return, a number of specific goals have been defined for C4. The goals of the C4 Mission are: to determine the elemental, molecular, and isotopic composition of a cometary nucleus; to characterize the chemical composition and processes in a cometary coma; and to determine the size, shape, morphology, mass, density, and rotational properties of a cometary nucleus.

Accomplishing these goals requires the fulfilling of a number of mission objectives. These can be divided into several categories depending on their importance to directly address the mission goals. The core objective of the C4 Mission is to determine the composition of a cometary nucleus by measuring the composition of the coma dust, including both the organic and silicate fractions, and the coma volatiles, including neutral gases, ions and ice grains. In addition, C4 will measure the dust-to-gas ratio for the comet and cosmochemically significant isotopic ratios.

Secondary objectives of the C4 Mission are to characterize the cometary nucleus by measuring its size, shape, surface morphology, mass, bulk density, and rotational properties, and to look for variations in coma composition as a function of time and nucleus activity.

Lower priority, opportunistic objectives are to observe the sources of nucleus activity, i.e., jets, and their variation over time, and to search for compositional heterogeneity on the cometary nucleus. In addition, as part of its baseline mission, the C4 spacecraft will fly by and observe the main belt, asteroids 598 Octavia and 2232 Altaj en route to the rendezvous with periodic comet Tempel 2.

## C4 Instrumentation

To obtain the data necessary for fulfilling the mission objectives, C4 will carry four instruments. The organic and inorganic chemical composition of the grains and gases emitted from the cometary nucleus will be analyzed by two science instruments: a mass spectrometer for the gas-phase constituents and a combined gas chromatograph and x-ray fluorescence analyzer for particulates. Both the Neutral Gas and Ion Mass Spectrometer (NGIMS) and the Cometary Ice and Dust Experiment (CIDEX)<sup>1</sup> instruments were under intensive development for the Comet Rendezvous/ Asteroid Flyby (CRAF) mission, and had been not only chosen for the mission in the original selection process, but survived all peer-reviewed instrument cuts prior to the mission cancellation. NGIMS will analyze molecules and ions over the mass range 1 to 150 AMU via quadrupole mass spectrometry. The C4 mini-Cometary Ice and Dust Experiment (m-CIDEX), an advanced, streamlined version of the CRAF CIDEX, captures and analyzes dust and ice grains streaming from the comet using X-Ray Fluorescence(XRF) and pyrolysis Gas Chromatography-Ion Mobility Spectrometry (GC-IMS). Two engineering instruments are also included in the C4 payload, the mini-Cometary Dust Experiment (mini-CODEM) and a Navigation Camera (NavCam), both of which will return extremely important science data as well. The

CRAF-derived mini-Comet Dust Environment Monitor (CODEM)<sup>2</sup>, will make extensive measurements of the dust flux and size distribution at the spacecraft, both as a means of assessing spacecraft safety and to obtain temporal and spatial data about the activity of the comet. The NavCam, although primarily to support optical navigation in the vicinity of the comet (and for asteroid flybys), will obtain extensive temporal morphology and topography of the comet nucleus and coma as well as identify active areas and rotational properties.

## EXPERIMENTAL

### Mini-Cometary Ice and Dust Experiment (m-CIDEX)

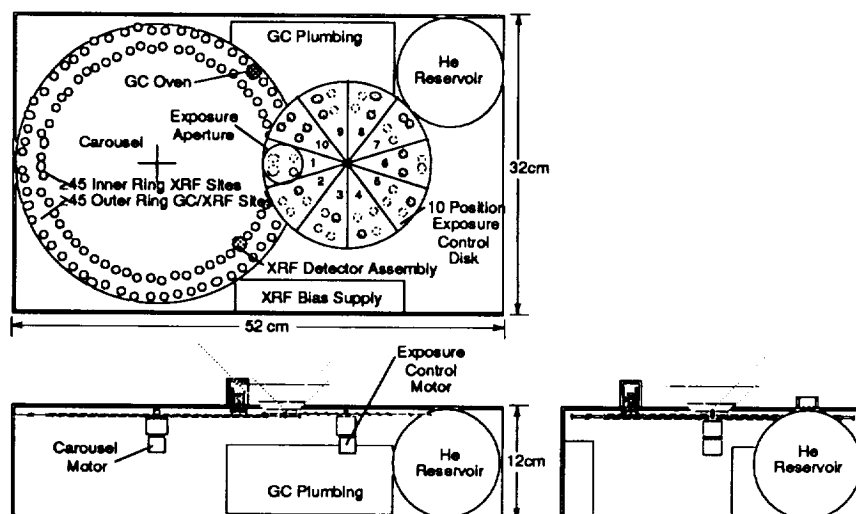


Figure 1. m-CIDEX Apparatus.

The m-CIDEX, shown in figure 1, will return data obtained from the collection and analysis of cometary dust and ice released from the comet. Using highly developed dust collection technology developed by Clark<sup>3</sup>, multiple samples representative of temporal and spatial distributions about the comet are collected. These samples are correlated to the dust flux measurements and orbital position. Collection Planchets utilize specially selected viscid surfaces and metal maze traps as universal particle collectors for the XRF and GC analyses, respectively. Other collectors include accordion traps, ultraclean metal foils, and a unique oil-impregnated filter combination. After collection periods from hours to days, the dust is subjected to analysis by X-Ray Fluorescence (XRF) spectrometry to obtain elemental composition of the bulk dust sample. The mini-CIDEX XRF determines elemental composition for carbon and all higher elements in the periodic table, with detection limits as low as 10 ppm for some elements. That sample or a similar sample can then be subjected to pyrolysis Gas Chromatography - Ion Mobility Spectrometry (GC-IMS) to obtain chemical composition, with particular emphasis given to the analysis of volatiles and organic molecules. The m-CIDEX GC-IMS (figure 2) detects less than 1 ppm of many inorganic and organic species, spanning the range from 2-atom molecules up to typical 8-carbon complex molecules. The sample can be step-wise pyrolyzed at various temperatures up to 1100K and then be returned to the XRF spectrometer after treatment to further enrich the analytical data. Table 1 shows the science requirements and capabilities of m-CIDEX. Molecular species in the cometary ice and dust grains that the GC-IMS experiment in m-CIDEX will focus its analyses on are shown in Table 2.

Feature	Requirements and Capabilities
<b>m-CIDEX Sample Collection And Transportation (SCAT) equipment:</b>	
GC Sample Collection Sites	≥45 Sites Heatable to ≥800°C in GC oven with temperature measurement.
XRF Sample Collection Sites:	≥45 Low Temperature Sites
Site Collection Temp.:	-110°C ≤ T ≤ 50°C
<b>m-CIDEX X-Ray Fluorescence (XRF) spectrometer:</b>	
Targeted Measurable Elements:	C, O, Na, Al, Cl, K, Ti, Zn, Mg, Si, S, Ca, Mn, Cr, Ni, Fe, Br, Sr, Zr, Ga, Se, Ge, V
Sample Quantity:	0.1 to 10,000 µg/cm <sup>2</sup>
Accuracy:	±10% from 0.5 to 10,000 µg/cm <sup>2</sup>
Sensitivity:	0.1 to 10 µg/cm <sup>2</sup> of O, Mg, Si, S, Ca, Cr, Mn, Fe, Ni
<b>m-CIDEX Gas Chromatograph - Ion Mobility Spectrometer (GC-IMS):</b>	
Measurable Species:	Hydrocarbons, nitriles, fixed gases, alcohols, aldehydes, amines, amino acids
Sensitivity:	1 × 10 <sup>-14</sup> moles/s or 1ppm in collected samples
Dynamic Range:	10 <sup>7</sup> for light gases, 10 <sup>4</sup> for medium organic compounds
Accuracy:	± 1% @ > 100 X sensitivity

**Table 1. Science Requirements and Capabilities of m-CIDEX.**

Hydrocarbons		Nitriles	Inorganics	Alcohols, Aldehydes	Amines, Amino Acids
CH <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>	CH <sub>3</sub> CN	H <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub>	CH <sub>3</sub> OH	CH <sub>3</sub> NH <sub>2</sub>
C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CH <sub>3</sub> CH <sub>2</sub> CN	NH <sub>3</sub> , H <sub>2</sub> O	CH <sub>3</sub> CH <sub>2</sub> OH	NH <sub>2</sub> CH <sub>2</sub> COOH
CH <sub>2</sub> CCH	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	CHCCN	HCN, CO, NO	CH <sub>2</sub> O	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub>
CH <sub>2</sub> CHCH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	C <sub>2</sub> N <sub>2</sub>	H <sub>2</sub> S, Ar,	CHOOH	NH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>
1,3-CH <sub>2</sub> CCHCH <sub>3</sub>	1-CHCCH <sub>2</sub> CH <sub>3</sub>		SO <sub>2</sub> , CO <sub>2</sub> , Ne	CH <sub>3</sub> CH <sub>2</sub> OH	
1-CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>				
CH <sub>2</sub> CHCH <sub>2</sub> CH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>				

**Table 2. Some Candidate Molecular Species in Cometary Grains.**

### **m-CIDEX GC-IMS Breadboard**

Laboratory versions of the m-CIDEX GC-IMS functional components are assembled in a breadboard for testing and evaluation. As shown in figure 2, the m-CIDEX GC-IMS breadboard currently uses three columns: 1) a light gas column; 2) an organic column; and 3) a polar column. Operating parameters for the columns and their associated detectors are shown in figure 3. The detectors are NASA developed, Modulated Voltage<sup>4</sup> Tri-axial Metastable Ionization Detectors (MIDs)<sup>5</sup>. A Keithly 247 supplies power to the MIDs and a Keithly 642 Electrometer monitors and displays detector current. Stock helium is used to purge the VICI 8 port valve used for sample introduction. GC carrier gas is Research Grade (99.9999%) helium passed through a VICI gas purifier. The IMS is a PCP Model 111, Dry Helium IMS<sup>6</sup> using a drift gas flow of 100ml/min and operating at 100°C. IMS drift gas is Research Grade helium (99.9999%) passed through a Mol. Sieve trap (cooled by a NessLab Cryocool CC-100II to -84<sup>0</sup> C) for further removal of water. Sample introduction to the IMS is via the GC column and MID. Data from the GC are interfaced through a Nelson Analytical Series 900 to PC Work Stations. PE Nelson Mod. 2600 Multiple Inst. Chromatography Software and Graseby Analytical Ltd. System V200 are used for the GC and IMS data, respectively.

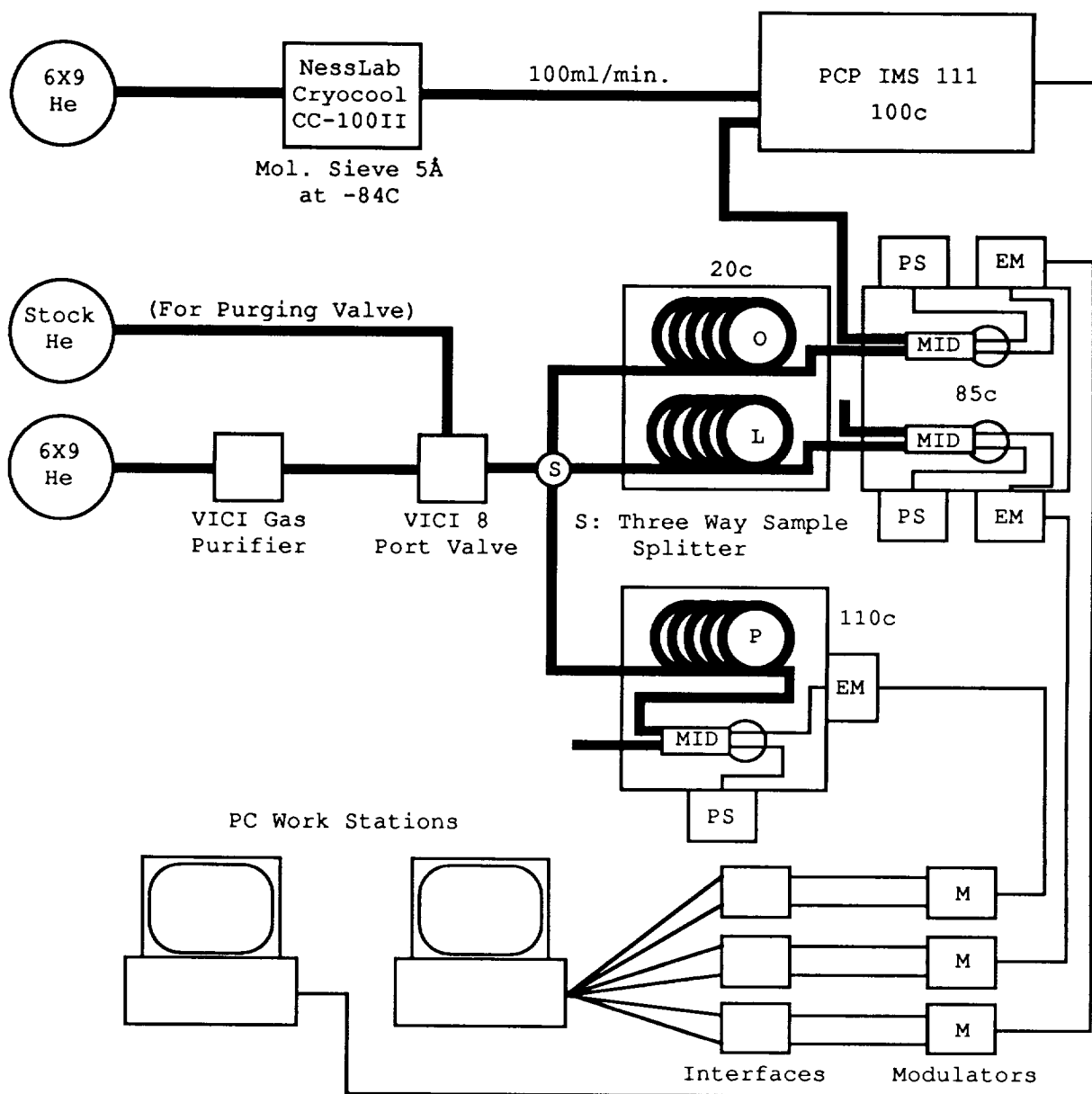


Figure 2. C4 m-CIDEX GC-IMS Breadboard.

**L (Light Gas)**

Hayesep A, 100/120 mesh,  
7.3m(L) x 1.08mm(ID), 304 SS  
Carrier Gas Flow Rate: 12.5ml/min.  
Column Temperature: Room.  
Detector Temperature: 85C.  
Applied Voltage: -320V.

**O (Organic)**

P-tolylisocyanate Porasil C, 100/200 mesh,  
1.15m(L) x 1.08mm(ID), 304 SS Column.  
Carrier Gas Flow Rate: 11.6ml/min.  
Column Temperature: Room.  
Detector Temperature: 85C.  
Applied Voltage: -275V

**P (Polar)**

Hayesep P, 140/170 mesh,  
2.13m(L) x 1.08mm(ID), Nickel column.  
Carrier Gas Flow Rate: 12.4ml/min.  
Column Temperature: 110C.  
Detector Temperature: 110C.  
Applied Voltage: -300V

**Figure 3. GC operating parameters.**

Samples are prepared in 1 to 3 liter stainless steel gas cylinders by simple dilution using Research Grade helium. An Exponential Dilution Flask sample dilution system will be used for wide range calibration studies. A 250 $\mu$ l sample loop is loaded and then flushed with carrier gas to introduce sample to the GC. The carrier gas, with sample, is then split into three streams, one for each column.

## **RESULTS AND DISCUSSION**

The maturity of the C4 analytical instruments is very high, largely due to extensive research and development in preparation for the CRAF Mission. For the m-CIDEX in particular, there is no further significant instrument development planned. Various versions of GC columns are now being tailored for this specific mission. The columns now being used are all of the packed variety, but other types of columns, such as *in situ* polymerized PLOT columns<sup>7</sup> are being considered. Although the IMS was not a part of the CRAF development efforts, it was developed through NASA's Small Business Innovative Research Program to analyze extraterrestrial volatiles from a gas chromatograph for planetary missions<sup>8</sup>, and was an analytical component on the Titan Aerosol and Gas Experiment (TAGEX) proposed for the Cassini Mission to Saturn and its moon Titan.

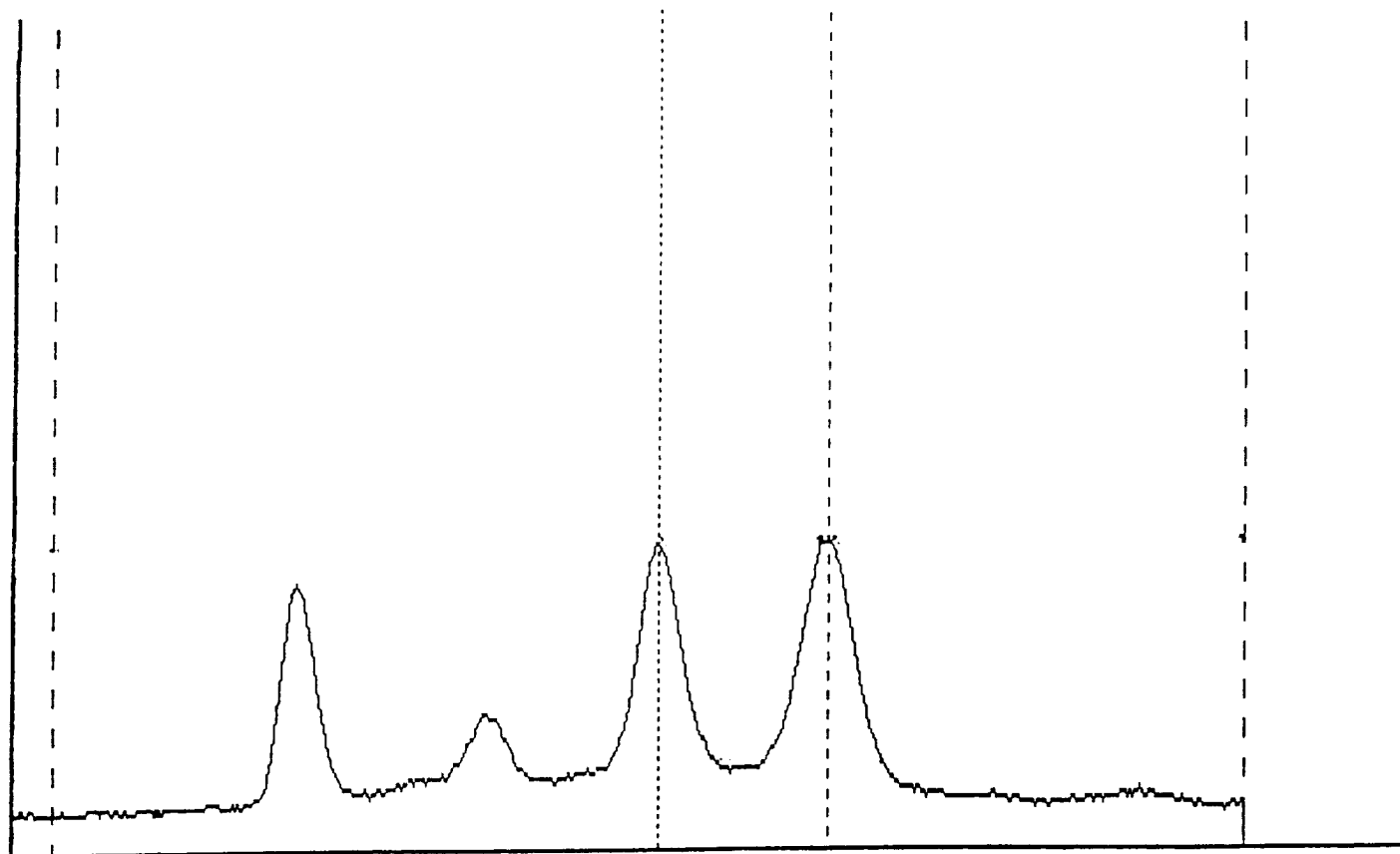
Current research efforts on the m-CIDEX GC-IMS are focused on the various combinations of molecular species that must be analyzed during C4's encounter with the comet. The GC-dry helium IMS has been successfully used to detect and provide spectra of samples in each of the target groups: Hydrocarbons, Nitriles, Inorganics, Alcohols and Amines. The first mixtures to be separated and analyzed on the m-CIDEX GC-IMS were hydrocarbons. Figures 4 and 5 show the IMS spectra of Butane and Ethylene during an analysis of 10 hydrocarbons by the m-CIDEX GC-IMS. The response of the IMS in these cases is typical for dry helium IMS response to simple hydrocarbons. A full chromatogram, showing the MID response, of this analysis is shown in figure 6

surrounded by the IMS spectra of all the components. In this case the column performed well and made the jobs of the MID and IMS easy. However, future analyses will combine sample species from more than one group, complicating the analysis and making complete gas chromatographic resolution of every component unlikely.

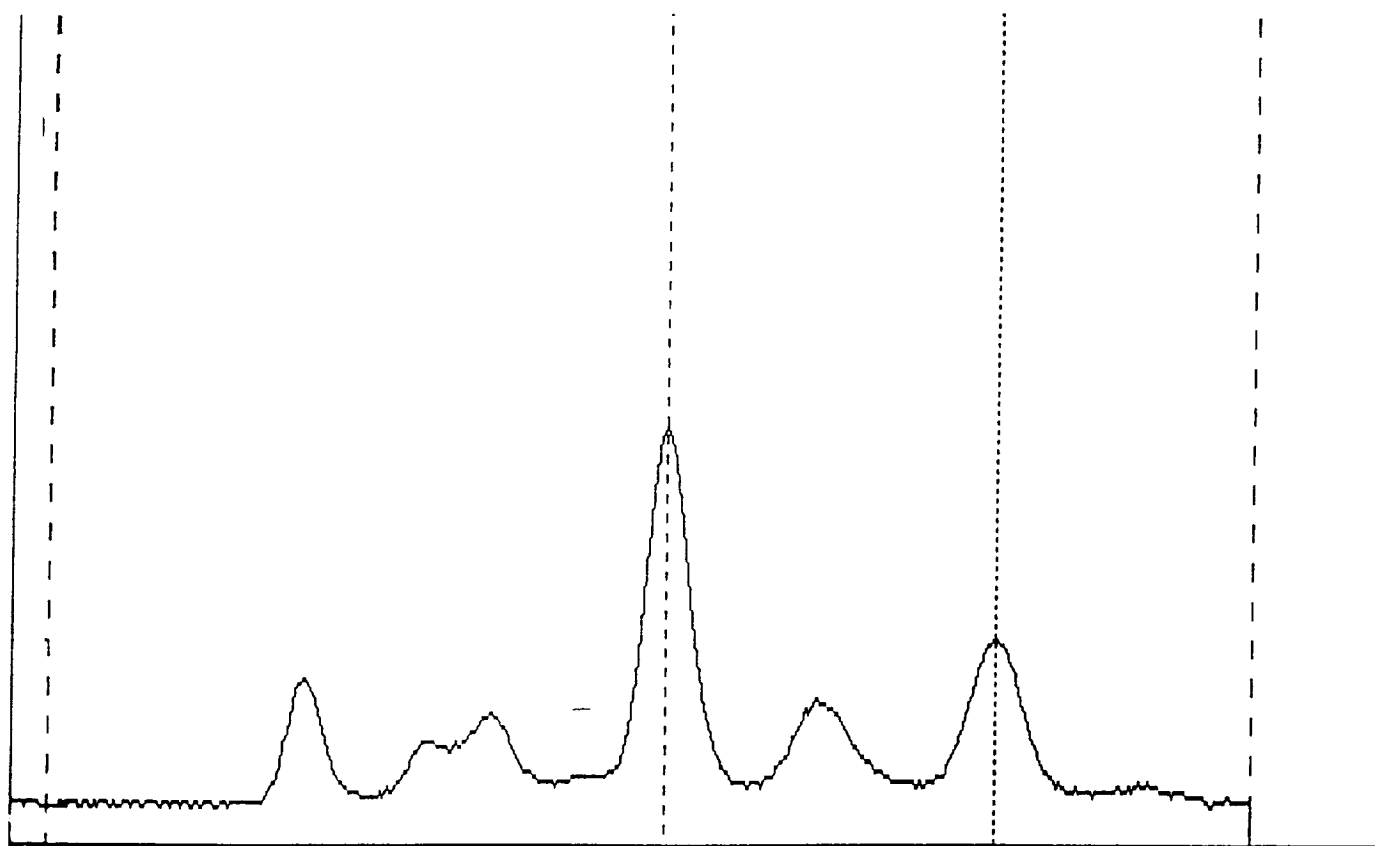
As the flight column(s) are selected, further tests of the GC-IMS on various, more complex, mixtures will be done. Addition of the sample collection system and pyrolysis ovens will then enable a full simulation of C4 m-CIDEX GC-IMS analyses to be performed.

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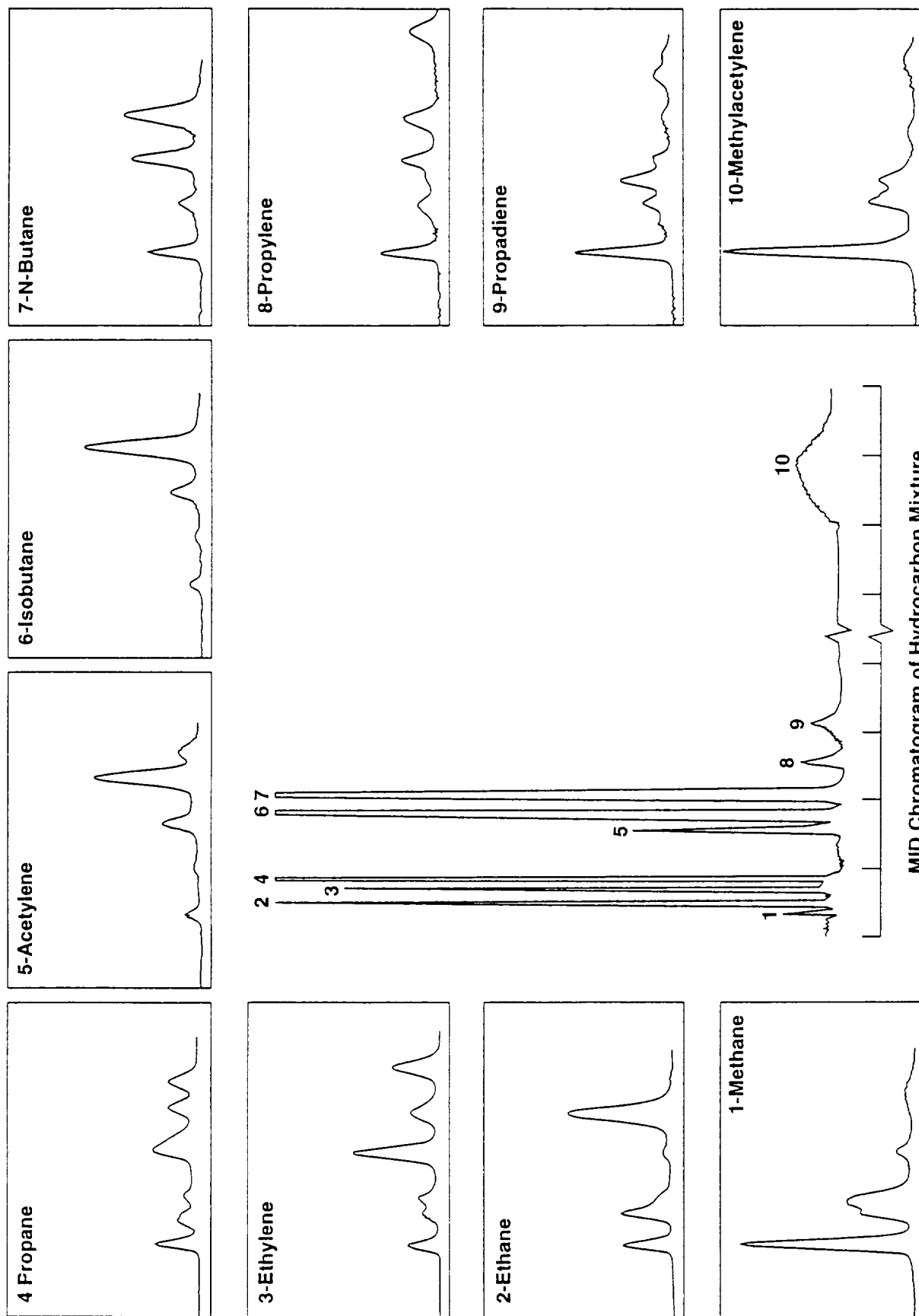


**Figure 4. Butane IMS spectrum taken from ten hydrocarbon mixture.**



**Figure 5. Ethylene IMS spectrum taken from ten hydrocarbon mixture.**





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Figure 6. M-CIDEX GC-IMS analysis of ten hydrocarbon mixture.